PREPARATION AND USE OF NIOBIUM CARBIDE ARTICLES

O. P. Kolchin and I. K. Berlin

N 65-36760

FACILITY FORM 602

(ACCESSION NUMBER)   (THRU)

(PAGES)   (CODE)

(NASA CR OR TMX OR AD NUMBER)   (CATEGORY)

PREPARATION AND USE OF NIOBIUM CARBIDE ARTICLES

O. P. Kolchin and I. K. Berlin[1]

ABSTRACT

36760

Two variants are presented of the method of manufacturing
from niobium carbide large-dimension parts for use chiefly as
heaters and other furnace parts. An experimental industrial
high-temperature induction vacuum furnace was tested, having
heaters and screens made of niobium carbide. The height of
the working space of the furnace was 1.3 m, the inner diameter
0.25 or 0.18 m. The heaters and screens were tested at tem-
peratures up to 2,770°K, and it was shown that it is possible
in principle to use parts made of niobium carbide in industrial
high-temperature induction vacuum furnaces.

The authors show that it is possible to raise the working
temperature of furnaces with graphite heaters by applying
carbide coatings to them or using screens made of niobium or
tantalum carbide.

The present study involved the development of a technological   /25*
process for the preparation of large-size articles from niobium carbide,

_____

*Numbers given in the margin indicate the pagination in the original foreign
text.

[1]Giredmet, Moscow

primarily heaters and shields for high-temperature industrial induction vacuum furnaces used for heat-treating chemically active metals.[2]

Among induction and resistance furnaces, vacuum furnaces with graphite or tungsten heaters are usually employed. However, the volatility of graphite at high temperatures in vacuum and also the risk of contaminating with carbon the metal being treated in the furnace do not permit its use above 2,000-2100°K. Vacuum furnaces with tungsten heaters cannot be used under industrial conditions either because of their low capacity (furnaces of type TVV-IVM) or because of contamination of the metal treated in the furnace with volatile oxides of tungsten and zirconium, which are evolved by the heater and the lining, as was the case with the vertical induction furnace of type OKB-530 at 2600°K with a tungsten heater and a zirconium dioxide heat insulation.

For this reason it became necessary to replace graphite and tungsten with some other refractory material whose use would eliminate the risk of contaminating the metals treated in the furnace. Among the refractory materials potentially suitable for use as heaters in high temperature furnaces, transition metal carbides are of interest. We choose niobium carbide, which has the following valuable properties (ref. 1): melting point, 3773°K; electrical resistivity, $0.74.10^{-6}$ ohm m; density, 7560 kg/m^3; microhardness, $23 \cdot 10^8$ dkN/m^2; thermal conductivity, 0.142 W/m deg; elastic modulus, $33.8 \cdot 10^4$ dkN/m^2.

Even at temperatures above 2,273°K, carbon diffuses into niobium carbide very slowly. For this reason, if the vaporization of carbon is appreciable when carbide heaters are used, a graphite heat insulation or shields of niobium carbide can be used in furnaces with a graphite heater.

[2]S. I. Romanov, K. S. Nizharadze, I. I. Vorob'yev, V. V. Shishkov, Ye. A. Yudin, Yu. F. Balyasov and V. M. Golankin participated in the work.

In order to make sure that niobium carbide can be used as the heater in
a high-temperature furnace, rods 10 mm in diameter were prepared under labora-
tory conditions from a powder with a particle size of ≤ 5 mμ by the
powder metallurgical method, and their mechanical and electrical properties
were determined. The transverse strength of samples sintered at 2,373°K was
274 MN/m^2, σ of compression was 288.3 MN/m^2 and the electrical resistivity
measured at room temperature was $0.4 \cdot 10^{-6}$ ohm m, and at 1,273 and 2,373°K,
respectively 1.6 and $3 \cdot 10^{-6}$ ohm m (according to the data of VNIIETO).

The niobium carbide rods were successfully tested by passing an electric
current through them in a resistance furnace at temperatures up to 3,273°K; even
at such high temperatures, no appreciable vaporization of the carbide was
observed. Preliminary results of laboratory experiments confirmed the
desirability of the development of a technological process for preparing
large-size heaters and other furnace parts from niobium carbide.

It should be noted that data on the technology of preparation of large-
size articles are practically nonexistent in Soviet and foreign literature.
A paper was published in 1959 (ref. 2) concerning the use of niobium and
tantalum carbide at temperatures above 1,773°K in the form of inserts,
measuring $14 \cdot 14 \cdot 14$ cm, for the protection of the graphite heater in a vacuum
device used for the gas-phase coating of plastics with an aluminum film.
References 3 and 4 are also devoted to the preparation of small-size compact
articles from niobium carbide.

Testing of Various Methods of Preparing Articles from Niobium Carbide

The articles were formed by using niobium carbide obtained by a process
developed earlier by carbidizing niobium pentoxide in a Tammann furnace (ref. 5).

The experimental batches of niobium carbide contained 88.5-90.3 percent niobium, 9-11 percent carbon, 0.1-0.3 percent oxygen, and about 0.3 percent nitrogen. The carbide powder passed completely through a sieve with a 150 mμ screen; the 50 mμ fraction comprised 50-80 percent. The density of the granular carbide was $2.8 \cdot 10^3$ kg/m³, and the weight was $4.6 \cdot 10^3$ kg/m³. The portion of the carbide with a coarseness of +50 mμ was additionally ground in a jet mill into a powder with a coarseness of ≤ 5 mμ.

Pressing. To obtain compact blanks from the niobium carbide, the latter was pressed into bars $10 \cdot 10 \cdot 70$ mm without a lubricant and also with various types of lubricants. The compact obtained with a pressure of $9.8 \cdot 10^7 - 49.03 \cdot 10^7$ N/m² had a low strength; a higher specific pressure (up to $98.1 \cdot 10^7$ N/m²) caused the formation of lamination cracks.

The possibility of obtaining compacts by vibropressing methods and continuous pressing at $423°K$ with the use of a phenol-formaldehyde resin was also determined. However, compacts of satisfactory quality could not be obtained from niobium carbide. The brittleness and high hardness of the niobium carbide crystals, the spherical shape of the particles, and the high weight per m³ as well as difficulties in the pressing of large-size compacts caused unfavorable conditions for pressing and made it necessary to resort to other unrelated forming methods.

Sintering in Molds. Sintering of niobium carbide powder of various grinding finenesses (-150, -50 and ≤ 5 mμ) was tested. The niobium carbide powder was poured into a graphite vessel (d_{inner} = 10 mm), was compacted by shaking, then sintered in a tubular graphite resistance furnace in a hydrogen medium at $2078°K$.

TABLE 1

Coarseness of initial carbide powder, μm	Transverse strength σ_{tr}, MN/m^2	Compressive strength σ_c, MN/m^2
≤ 150 (including 77% of powder ≤ 50)	36.3-69.6	-
≤ 50	65.7-122	127.5
≤ 5	219.7	214.8

Table 1 lists data on the strength of the sintered specimens
obtained by sintering niobium carbide of various grain sizes. Despite the
appreciable scatter of these data, apparently caused by the presence of micro-
cracks, they definitely indicate that sintering of the unpressed niobium
carbide powder can produce sufficiently strong specimens. The values of the
transverse and compressive strength of the sintered specimens increase with
the degree of comminution of the initial niobium carbide. The strongest
specimens were those sintered from carbide with a grain size of no more than
5 mμ.

The influence of temperature on the sintering of niobium carbide with
a grain size of -50 and -5 mμ was then studied in the 1,200-2,373°K range.
The course of the process was followed by means of the shrinkage and change in
porosity, electrical resistance, transverse strength and compressive strength,
which were measured at 293°K on specimens sintered at a given temperature.
The data obtained are shown in table 2 and in figures 1 and 2. As was to be
expected, the sintering of powders with a grain size of -5 mμ begins at lower
temperatures and is more complete than that of powders measuring -50 mμ.

For example, the transverse strength of the specimen sintered at 1,473°K
from -5 mμ carbide turned out to be 7 times higher than that of the specimen

TABLE 2

Sintering temperature, °K	Carbide of -50 mμ coarseness					Carbide of -50 mμ coarseness				
	Volume shrinkage, %	Porosity, %	Strength, MN/m² σ_{tr}	σ_c	ρ, ohm m·10⁶ at 20°C	Volume shrinkage, %	Porosity, %	Strength, MN/m² σ_{tr}	σ_c	ρ, ohm m·10⁶ at 20°C
1223	10.2	-	-	-	-	12.2	33.3	-	-	-
1273	-	30.2	-	38.2	5-5.5	-	-	125.5	-	2.4
1373	11.9	-	-	54.9	-	17.0	25.3	-	-	1.9
1473	-	26.8	23.5	-	5.4	29.7	19.9	166.7	119.6	2.0
1573	-	-	30.4	-	4.6	-	12.4	182.4	-	1.8
1673	-	22.6	34.3	106.9	3.6	-	-	-	176.5	-
1773	20.8	-	-	168.7	3.0	-	12.3	219.7	-	1.4
1873	21.3	21.4	42.2	-	3.0	38.8	13.8	-	-	1.4
1973	21.8	-	44.1	-	3.0	37.5	11.4	-	-	1.5
2073	-	-	65.7	-	-	-	-	-	-	1.4
2373	-	-	-	-	-	-	-	273.5	288.3	0.4

6

Figure 1. Porosity and shrinkage
of niobium carbide of -50 and -5
mμ coarseness vs. sintering
temperature.

Figure 2. Transverse and compressive
strength and electrical resistivity of
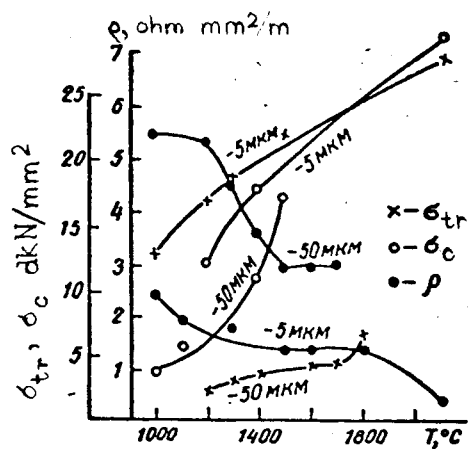niobium carbide of -50 and -5 mμ coarse-
ness vs. sintering temperature.

sintered from -50 mμ powder at the same temperature and 2.5 times greater than
that of the specimen prepared from the same powder at 2,073°K. The volume
shrinkage, whose change often serves to determine the course of the sintering

process, is 12.2 percent at a low of 1223°K, sharply increases at 1373 and 1,473°K, and reaches 38 percent at 1,873-1,973°K (which is twice as much as for the coarser powder). A corresponding decrease is observed in the porosity and electrical resistance of the specimens, equal, respectively, to 11.4 percent and $1.5 \cdot 10^{-6}$ ohm m in the case of sintering at 1,973°K, which is one-half as much as for the -50 mμ powders.

Forming with the use of Phenol-Formaldehyde Resin. This resin, /28 widely employed in the production of plastics, was tested as a binder in the preparation of articles from niobium carbide. Preliminary qualitative data on the behavior of niobium carbide in a mixture of the phenol-formaldehyde resin, taken in the amount of 5 and 10 mass percent, showed, during heating to the polymerization temperature of the resin, that the mixture forms a compact mass, assumes the outlines of the mold, and has a mechanical strength sufficient for removal from the mold and transportation to the furnace for subsequent heat treatment. When 10 percent of the resin is added, a mass is obtained that is stronger than when 5 percent of the resin is added, but it shows the presence of many larger pores.

A study of the porosity of the specimens obtained by sintering -50 mμ carbide containing 5 percent of resin as a function of sintering temperature showed that the specimens have an intercommunicating porosity, and as the sintering temperature rises from 1,600 to 3,000°, no sharp decrease in porosity occurs, since the free carbon remaining in the carbide upon decomposition of the resin and the large number of branched pores interfere with the growth of grains and with the packing of the material. After sintering at 3,273°K, the total porosity of the specimens was about 40 percent.
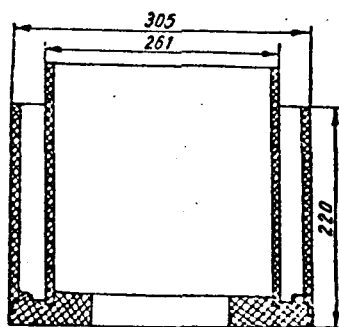
Figure 3. Graphite mold for carbide rings.

Preparation of a Heater and Shields for a High Temperature Induction

Furnace from Niobium Carbide

An OKB-530 furnace of VNIIETO design proved unsuitable for the thermal

treatment of a chemically active metal at 2,300° under industrial conditions.

For this reason, it appeared advisable to replace the tungsten heater with a

carbide heater, the zirconium dioxide lining with graphite grit, and the

zirconium dioxide shields with niobium carbide disks. The heater had to be

made of carbide rings 300/350 mm in diameter so that they could form a stack

1500 mm high, and the carbide shields were made in the shape of disks   /29

320 and 240 mm in diameter and 20-50 mm high. Both of the methods of forming

considered above (with the resin and without the binder) were employed.

Forming of Rings and Disks with the use of the Phenol-Formaldehyde Resin.

Niobium carbide mixed with the phenol-formaldehyde resin taken in the amount of

5 mass percent were poured into the circular slot of a graphite mold (fig. 3)

and compacted by shaking. The inner graphite tube, which was first wrapped in

a layer of dense paper glued at the seam, was removed from the mold after

compacting the carbide, the paper tube being left in its place. When shields

were prepared in the shape of disks, graphite vessels of the corresponding

dimensions served as the mold. The charge compacted in the mold was placed
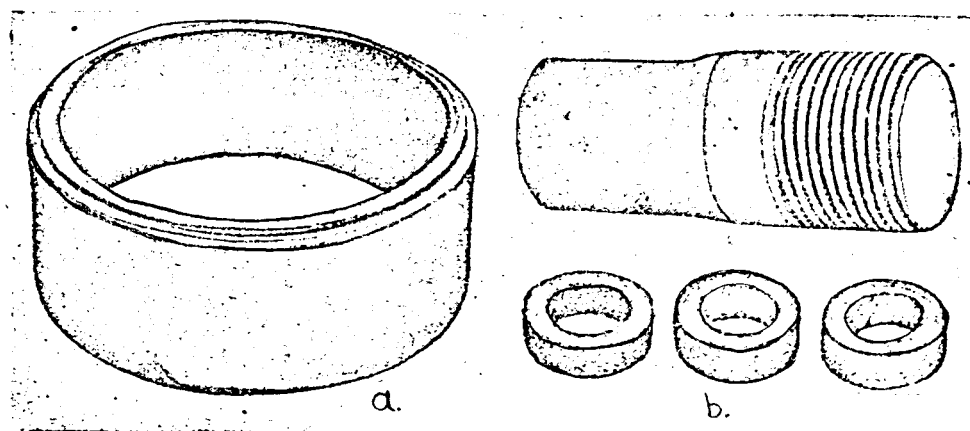
Figure 4. Niobium carbide articles: a, ring ⌀ 300 mm;

b, rod with thread and bevel, rings ⌀ 35 mm.

in a vacuum drying oven in which the resin polymerized at 423-453°K in air.

The binder was then partially removed in this oven in a vacuum at 573°K.

After cooling in the oven, the carbide rings and disks were taken out of the mold and annealed in hydrogen at 1,873°K in a graphite resistance furnace. The shrinkage of the articles, which was very slight during sintering, begins at 1,473° and practically ends at 1,873°. The total shrinkage is 2-3 percent along the height and 1-5 percent along the diameter.

After sintering at 1,873°, the articles are machined by cutting or grinding. This made it possible to cut a circular groove on all the carbide rings from which the shaft of the furnace was made. Figure 4 shows a ring 300 mm in diameter, a rod with a thread and bevel and rings 35 mm in diameter. Further sintering of the rings and disks was performed in a vacuum with induction heating up to 2,350°C. Figure 5 shows a line diagram of the production of the articles from a mixture of niobium carbide with the phenol-formaldehyde resin.

```
                    Niobium           Phenol-formal-
    Hydrogen        carbide           dehyde resin
   ──────────       ────────          ──────────────
       │               │                    │
       │               │                ┌─────────┐
       │               │                │ Grinding │
       │               │                └─────────┘
       │               │                    │
       │               │                ┌──────────┐
       │               │                │ Screening │
       │               │                └──────────┘
       │               │                    │
       │               ▼                    │
       │        ┌──────────────┐            │
       │        │    Mixing    │◄── 150 mμ resin
       │        └──────────────┘
       │               │
       │        ┌──────────────┐
       │        │  Mixture of  │
       │        │ carbide and resin│
       │        └──────────────┘
       │               │
       │        ┌──────────────┐
       │        │  Forming of  │
       │        │   articles   │
       │        └──────────────┘
       │               │
       │        ┌──────────────┐
       │        │  Heating at  │
       │        │ 150-180° in air│
       │        └──────────────┘
       │               │
       │        ┌──────────────┐
       │        │ Heating at 300°│
       │        │  in vacuum   │
       │        └──────────────┘
       │               │
       └──────►┌──────────────┐
               │Sintering at 1600°│
               │  in hydrogen │
               └──────────────┘
                       │
               ┌──────────────┐
               │  Mechanical  │
               │  treatment   │
               └──────────────┘
                       │
               ┌──────────────┐
               │ Sintering at ≥│
               │ 2100° in vacuum│
               └──────────────┘
                       │
                       ▼
                Niobium carbide
                   articles
               ──────────────
```
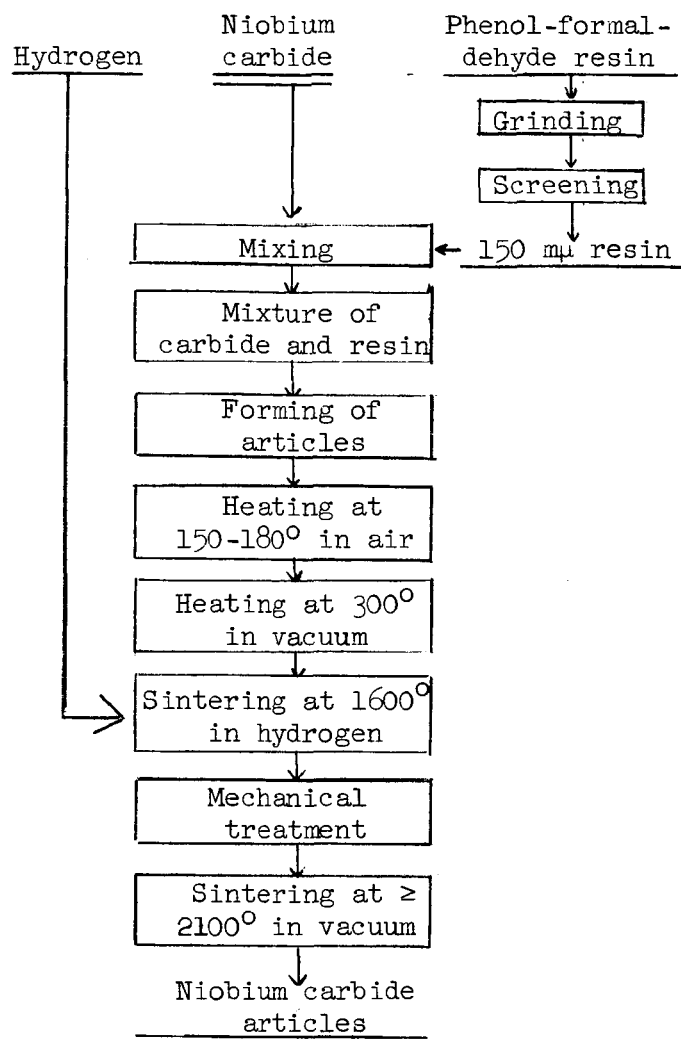
Figure 5. Diagram of preparation of niobium

carbide articles with use of phenol-formalde-

hyde resin.

Forming of Rings without a Binder. Niobium carbide powder with a grain

size of -50 mμ, compacted in the mold, was presintered at 1,470°K in

a graphite resistance furnace in a hydrogen medium. Preliminary experiments

established that in the case of a hydrogen medium, the sintered specimens

obtained are stronger than by sintering in a vacuum. This is explained by

the fact that in hydrogen there is a less extensive removal of iron, lower

oxides and other impurities from the carbide which apparently form a liquid phase in the presence of which the conditions of sintering of the carbide are improved. In addition, conditions for a more uniform heating of the articles are created in a hydrogen medium.

The second stage of the sintering consisted in heating the articles in a vacuum up to 2,273°K. As shown by preliminary experiments, during the sintering the upper part of the rings displays greater shrinkage than the lower part, which, being adjacent to the support, is subjected to the force of friction during the shrinkage. This causes the rings to warp and the formation of cracks. In order to reduce the irregularity of the shrinkage during sintering, a special device was proposed which makes it possible to sinter the ring in a horizontal position. Shrinkage was thus more uniform, the shape of the rings was closer to cylindrical, and no cracks were observed. The porosity of such rings amounts to 19 percent.

Assembly and Testing of Induction Furnace with Niobium Carbide
Heaters and Shields.

An Lts-42-type induction furnace with niobium carbide heaters and <u>/31</u> shields was assembled from the housing, inductor and electric and vacuum system of an OKB-530-type furnace. The heater of the furnace 4 (fig. 6), 1500 mm high, made of carbide rings 150 mm high each, was mounted on a graphite base (9, 10). On the bottom, the working space of the furnace was shielded with niobium carbide disks (6), 320 and 240 mm in diameter and 50 mm thick; on the top, the space was shielded with a graphite vessel filled with graphite grit. Graphite grit (7) serves as the heat insulation of the furnace.
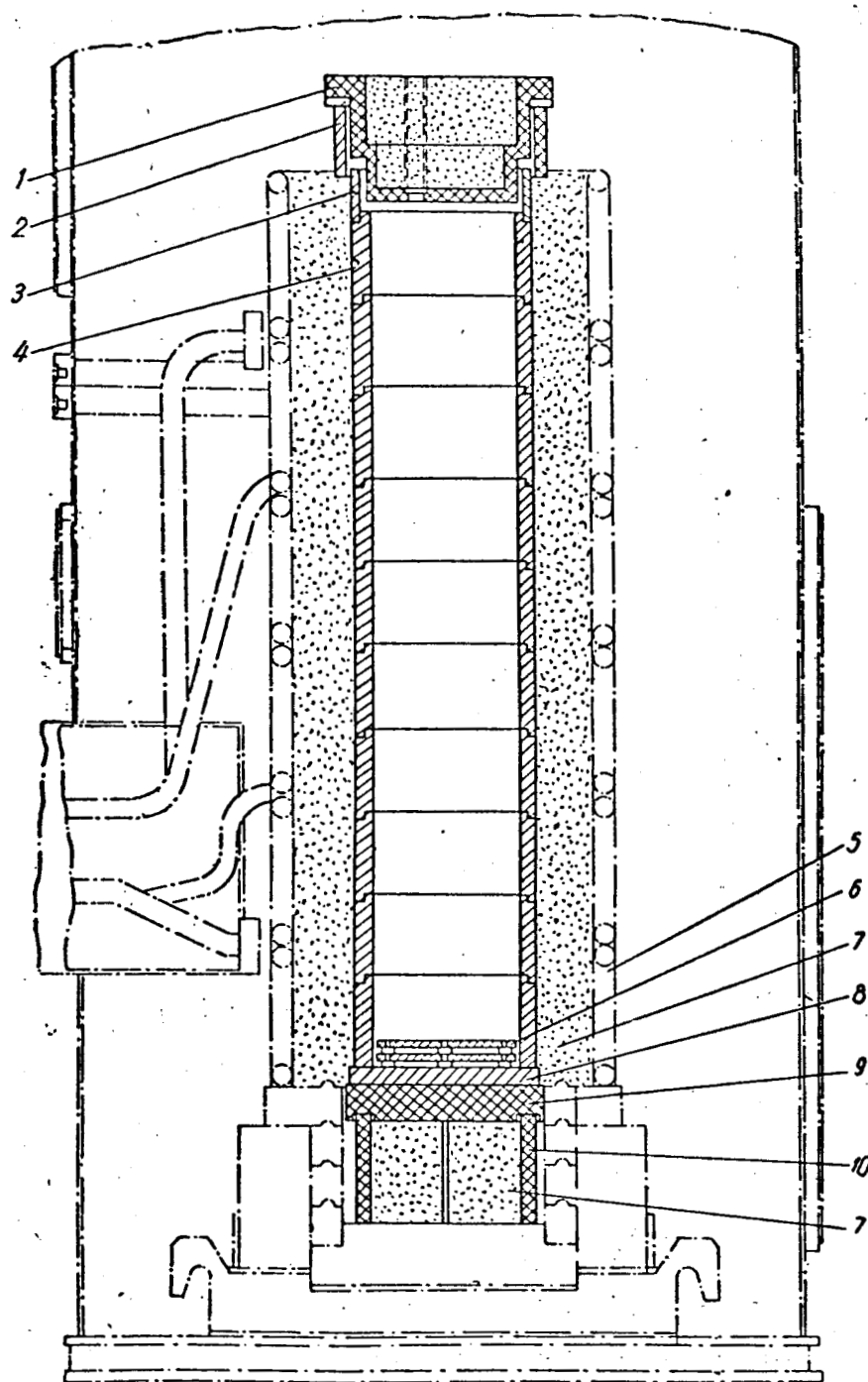
Figure 6. Diagram of furnace with carbide heater (LTs-42). 1, graphite plug; 2, 3, graphite rings; 4, graphite heater; 5, inductor; 6, carbide disks; 7, graphite grit; 8, carbide disk; 9, graphite disk; 10, graphite vessel.

13

A heater made of rings 300/250 mm in diameter, prepared from niobium carbide with the aid of the phenol-formaldehyde resin, was tested at temperatures up to 2,623°K. The temperature distribution at the heater was uniform: measured at three points along the height of the heater with an optical pyrometer, the the temperature gradient was 30-40°. The power expended by the furnace at 2,623°K was 120 W.

After heating at 2,423°K, the carbide rings of the heater contained up to 12.5 percent C (the carbon content at the stoichiometric composition NbC was 11.4 percent. The presence of free carbon in the carbide, caused by an incomplete removal of the binder, is undesirable, since its gradual removal during subsequent operation of the furnace may cause a contamination of the metal being sintered. Therefore, in order to partly remove the carbon from the metal, the inner surface of the rings was coated with niobium oxide from the gas phase. As a result of a further operation of the heater for 350 hr, the carbon content in a thin (1 mm) surface layer of the ring decreased to 8.9 percent. This could be explained by the dissociation of carbide (ref. 6,7) above 1,873°K and also by the interaction with lower oxides of the elements which volatilize from the metal subjected to the heat treatment during its vacuum refining. However, the simultaneous diffusion of carbon from the heat-insulating graphite packing should practically offset its removal from the surface layers.

The total duration of the heating of the furnace during its tests up to 2,423°K was 500 hr, including 150 hr at 2,173-2,423°K. When the temperature at the heater 300 mm in diameter was raised to 2,573°K and above, there was danger that the inductor might break down as a result of possible damage to the electrical insulation, since the 100 mm thickness of the heat-insulating graphite grit layer might have been insufficient for such high temperatures.

In order to increase the thickness of the heat-insulating layer between
the heater and the inductor to 145 mm, the heater was built up of rings 210/180
mm in diameter. These rings and shields in the form of disks 300, 250 and 160
mm in diameter were prepared from niobium carbide powder without using a binder
by sintering in accordance with the above-described process. The articles
obtained had a porosity of 10-20 percent and were mechanically strong. The
working space of the heater assembled from such rings 150-180 mm high was
shielded on the bottom and at the top by niobium carbide disks; the upper
shield had a perforation for measuring the temperature. A temperature of
$2,773^{\circ}K$ was reached at the heater. The capacity of the furnace was 170 kW.

Results of tests of LTs-42-type furnace showed that niobium carbide could
indeed be used as a heater for high-temperature vacuum induction furnaces.
Carbide heaters and furnace parts can be used at $2,773^{\circ}K$ and higher   /32
both in vacuum furnaces and in furnaces with an atmosphere of gases which do
not interact with the carbide.

The process of preparation of niobium carbide articles is applicable with
certain modifications to the preparation of articles from similar carbides,
for example those of tantalum (m.p. $4,153^{\circ}K$), zirconium ($3,803^{\circ}K$), hafnium
($4,433^{\circ}K$), and also binary carbides which are of great interest in high-
temperature technology.

Use of Niobium and Tantalum Carbide as Protective Coatings
in Graphite Furances

Niobium and tantalum carbide are characterized by a low solubility of
carbon therein (ref. 6), and for this reason they could be expected to act as
a diffusion barrier for carbon. To check this hypothesis, shielding of a

15

chemically active metal with tantalum carbide from contamination with carbon evaporating from the graphite heater was tested. A tantalum carbide layer 0.3 mm thick was smeared on the inner surface of a graphite tube, and the latter was fired with the coating at 2,473°K in a vacuum. A bar of the pure, highly active metal suspended inside the tube was then heated at a pressure of 0.133 N/m², and carbon content of the metal was periodically checked. The results of the experiment showed that the TaC coating 0.3 mm thick protects the metal for 6 hr from contamination by the carbon evaporating from the graphite tube at 2,423°K. During heating under the same conditions but without a carbide coating, the carbon content in the metal increased by 1-2 percent in 3 hr.

A similar protective effect is observed when graphite heaters are coated with niobium carbide. The use of such coatings of niobium pentoxide, deposited by smearing and also from the gas phase by vaporizing niobium oxide (with the conversion of the oxides into niobium carbide by the reaction with graphite) made it possible to raise the maximum permissible operating temperature of induction vacuum furnaces from 1,973 to 2,173°K under industrial conditions.

The use of thicker and denser carbide coatings should lengthen the duration of their protective action. A more effective protection from the carbon vaporizing off the heater into the working space may be achieved by means of carbide shields placed at some distance from the heater.

Such shields were prepared from niobium carbide in the form of rings 140 mm in diameter and 110 mm high in accordance with the process which we developed. Their tests at the VNIIETO at 2,473°K in a graphite resistance furnace gave positive results.

Summary

1. Two variants of a process of preparing large-size articles from niobium carbide for use as heaters and shields were developed. The first variant, which includes the use of the phenol-formaldehyde resin, may be recommended for the preparation of carbide articles of high porosity with a high carbon content; the second, which specifies the forming of dry carbide powders, is recommended for the preparation of low-porosity articles which contain practically no free carbon.

2. The use of niobium carbide rod heaters was studied in high /34 temperature resistance furances.

3. An experimental industrial high-temperature induction vacuum furnace of type LTs-42 with niobium heaters and shields was tested. The furnace was assembled on the basis of the OKB-530 furnace (designed by the VNIIETO). The height of the working furnace was 1.3 m and the internal diameter was 0.25 or 0.18 m.

4. It was shown that the working temperature of furnaces with graphite heaters can be raised by depositing carbide coatings or using niobium carbide shields.

REFERENCES

1. Kiffer, K. and Shvartskopf, P. Hard Alloys (Tverdyye splavy). Metallurgizdat, Moscow, 1957.

2. Holland, L. Vacuum, Vol. 6, 161, 1959.

3. Kislyy, P. S., Panasyuk, A. D. and Samsonov, G. V. Poroshkovaya metallurgiya, No. 2, 38, 1962.

4. Avgustinnik, A. I., Vigdergauz, V. Sh., Gropyanov, V. M. and Drozdetskaya, G. V., Poroshkovaya metallurgiya, No. 6, 11, 1963.

5. Kolchin, O. P., Sumarokov, N. V. and Berlin, I. K., Sb. nauchnykh trudov Giredmeta, No. 1, 712, 1959.

6. Fries, R. Vaporization Behavior of Niobium Carbide. J. Chem. Phys., Vol. 7, No. 2, 320, 1962.

7. Kolchin, O. P. Sb. nauchnykh trudov Giredmeta, No. 6, 56, 1962.